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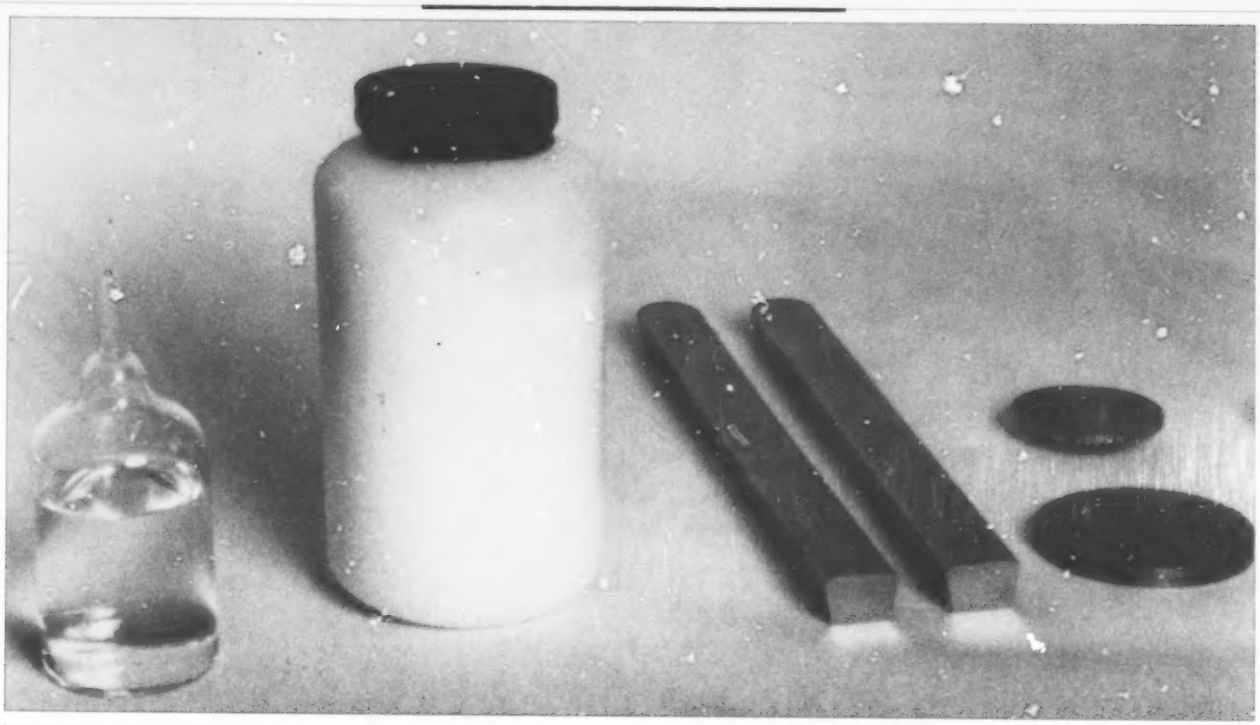

GERMANIUM

By Thomas O. Llewellyn

1989

U.S. DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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GERMANIUM

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Director

October 1990

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COVER PHOTO:
Germanium products. Shown (left to right) are an ampule of germanium tetrachloride, a bottle of germanium dioxide, two zone-refined (intrinsic) germanium bars, and a variety of optical grade germanium blanks. (Photo courtesy of Eagle-Picher Industries Inc.)

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GERMANIUM

By Thomas O. Llewellyn

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The estimated domestic refinery production and consumption of germanium decreased compared with the levels of 1988. Infrared systems and fiber optics continued to be the major end uses. The domestic fiber-optic market for germanium decreased for the fourth consecutive year and consumption for this application was about 25% less than that of 1988.

DOMESTIC DATA COVERAGE

Domestic refinery production and consumption data for germanium are estimated by the Bureau of Mines based on discussions with domestic producers.

LEGISLATION AND GOVERNMENT PROGRAMS

In September, the Defense Logistics Agency (DLA) contracted to purchase 9,000 kilograms of germanium metal in two separate and equal solicitations. DLA scheduled the first lot for delivery starting July through November 1990 and the second lot for the period between September 1990 and January 1991. The contract price for both lots was $609 per kilogram. DLA rejected bids ranging from $559 to $582 per kilogram received from European and African producers and selected Eagle-Picher Industries Inc. The main reason for the selection was a clause in the solicitation that indicated the agency may be required to follow a "Buy American" policy for the acquisition of strategic and critical materials that are mined and refined in the United States (Amendment No. 7, Public Law 98-473, October 12, 1984).[1]

STRATEGIC CONSIDERATIONS

The Federal Emergency Management Agency (FEMA) established the importance of germanium as a strategic and critical material on July 6, 1984, and an initial National Defense Stockpile (NDS) goal of 30,000 kilograms of germanium metal. Based on the U.S. Army's estimates for actual emergency conditions of mobilization, FEMA established a new goal of 146,000 kilograms on July 24, 1987.

Some of the metal inventory acquisitions made in 1988 were delivered in 1989 and, as of December 31, the stockpile inventory was 38,282 kilograms of germanium metal.

DOMESTIC PRODUCTION

The Bureau of Mines estimated domestic refinery production from both primary and secondary materials at 20,000 kilograms, a decrease of 5% compared with that of 1988.

Hecla Mining Co. bought the assets of St. George Mining Corp. of St. George, UT, for $5.5 million. St. George, a subsidiary of the Canadian company Musto Explorations Ltd. recovered and mined germanium and gallium as principal products until 1987 when it closed its operation. The new owners expected to resume mine and refinery production during the first quarter of 1990 and reach full production levels before yearend.

CONSUMPTION AND USES

The Bureau also estimated that consumption of germanium decreased about 10% compared with the level of 1988. The estimated consumption pattern by end use of germanium in 1989 was as follows: infrared systems, 65%; fiber optics, 6%; gamma-ray, X-ray, and infrared detectors, 8%; semiconductors, 8%; and other, 13%.

The largest end use for germanium continued to be in infrared optics, mainly for military use in guidance and weapon-sighting systems. Germanium containing lenses and windows transmit thermal radiation similarly to visible light transmission by optical glass. Germanium glass was also used for nonmilitary surveillance and monitoring systems in fields such as satellite systems and fire alarms.

The U.S. fiber-optic market for germanium continued the downward trend of the previous 3 years, and consumption of germanium in this application decreased about 25% compared with that of 1988. Germanium is used as a dopant in the core of many optical fibers employed in telecommunications. The decline resulted from the development of new manufacturing processes that achieved more efficient use of germanium.

American Telephone & Telegraph Co. (AT&T) of Morristown, NJ, and Kousai Denshin Denwa of Japan completed installation of a 8,271-mile underwater fiber-optic cable system that links the Guam, Japan, and the United States. This system, known as the Pacific Link, is capable of carrying 40,000 phone calls simultaneously. The underwater cable from Point Arena, CA, goes to an undersea branching unit offshore of Japan. At this point the cable splits, and one branch goes to Tanguisson, Guam, and the other to Chikura, Japan.[2]

AT&T and Zenith Electronic Corp. signed a joint agreement to develop a system for high-definition television (HDTV). This application was poten-

tially a large market for fiber-optic applications in transmission network.[3] Although not used in all fiber-optic systems, germanium is an important constituent in many fiber-optic cables.

Two of the U.S. Navy's guided-missile cruisers were outfitted with fiber-optic cable systems that transmit several voice and data functions, including combat system displays and a damage control sensor system. Fiber-optic cable for shipboard communications offered a dramatic advantage in terms of weight and immunity to electromagnetic interference compared to coaxial copper cable. As an example, a 750-foot coaxial cable for an advanced 3-D radar system weighing about 7 tons and measuring 18 inches in diameter can be replaced by a 40-pound fiber-optic cable measuring less than 1 inch in diameter. More information on the present market for fiber-optic components and their applications were described in the study "U.S. Navy Market for Fiberoptic Components," available from Kessler Marketing Intelligence, 31 Bridge Street, Newport, RI 02840.[4]

PRICES

Throughout 1989 domestic producer prices for germanium metal and dioxide, published by *Metals Week*, remained at the levels established in late 1981 ($1,060 and $660 per kilogram, respectively). However, discounting by producers was evident during 1989 because of competition from imported material.

The Belgian producer price for germanium metal, published by *Metal Bulletin* (London), remained throughout the year at about $754 per kilogram.[5]

FOREIGN TRADE

A comparison of the value per kilogram of imported germanium material with the published foreign producer price for germanium metal was used to estimate the germanium content of imported materials. In 1989, the estimated germanium content of total imports was calculated to be approximately 33,000 kilograms.

TABLE 1

U.S. IMPORTS OF GERMANIUM,[1] BY CLASS AND COUNTRY

Class and country	1988		1989[2]	
	Gross weight (kilograms)	Value	Gross weight (kilograms)	Value
Unwrought and waste and scrap:				
Australia	100	$33,960	—	—
Belgium	6,419	4,105,962	15,985	$12,027,567
Canada	88	54,337	2,407	1,470,524
China	1,986	1,184,120	3,195	1,607,868
France	3,949	2,154,821	7,973	5,313,134
Germany, Federal Republic of	244	162,147	3,421	1,145,407
Hong Kong	—	—	16	6,480
Israel	—	—	55	35,221
Japan	—	—	8	3,034
Netherlands	140	78,501	849	281,574
Singapore	—	—	15	8,503
Switzerland	—	—	3,260	182,166
United Kingdom	2,765	1,597,641	2,921	1,707,877
Total	15,691	9,371,489	40,105	23,789,355
Wrought:				
Belgium	2,646	3,211,285	—	—
France	259	191,942	—	—
Germany, Federal Republic of	254	330,467	—	—
Israel	78	36,233	—	—
Netherlands	54	49,821	—	—
United Kingdom	309	347,583	—	—
Total	3,600	4,167,331	—	—

[1] Because of the implementation of the Harmonized Tariff System in Jan. 1989, import categories for 1989 are not necessarily comparable with those in 1988.
[2] Beginning in 1989, only data for unwrought and waste and scrap are available.
Source: Bureau of the Census.

WORLD REVIEW

World refinery production was estimated at 82,000 kilograms. Primary germanium was produced by Métallurgie Hoboken-Overpelt S.A. (MHO), Belgium; Johnson Matthey Electronics, Canada; Société Minière et Métallurgique de Peñarroya S.A., France; Preussag AG and Otavi Minon AG, Federal Republic of Germany; Società Mineraria e Metallurgica di Pertusola Sud S.A., Italy; and Nippon Denshi Kinzoku and Sumitomo Metal Mining Co. Ltd, Japan. Germanium refineries also were in China and the U.S.S.R.

Capacity

The data in table 2 represent rated annual production capacity for refineries as of December 31, 1989. Rated capacity was defined as the maximum quantity that could be produced on a normally sustainable, long-term operating rate based on the physical equipment of the plant and routine operating procedures for labor, energy, materials, and maintenance. Capacity included both operating plants and plants temporarily closed that in the judgment of the author could be brought into production within a short period of time with minimum capital expenditure.

Refineries rated capacity of germanium was estimated based on discussions with some officials from private industry, past and present production rates, and published capacity data.

Brazil

Telebras, Brazil's state-owned telecommunications company, ordered 35,000 kilometers of optical fibers from Philips Optical Fiber, Eindhoven, the Netherlands. The optical fibers will

TABLE 2

WORLD ANNUAL GERMANIUM REFINERY PRODUCTION CAPACITY, DECEMBER 31, 1989

(Thousand kilograms)

	Capacity
North America:	
Canada	10
United States	45
Total	55
Europe:	
Belgium	50
France and Italy	35
Germany, Federal Republic of	35
Centrally planned economy countries	40
Total	160
Asia:	
China	10
Japan	35
Total	45
World total	260

be used by several Brazilian companies to manufacture fiber-optic cables, in great demand by the communications industry.[6]

Canada

Canstar Communications, a division of Canada Wire & Cable Ltd. of Toronto, Canada, was awarded a contract by the New York City Transit Authority to supply and install a fiber-optic communications network. This network will interconnect 107 transit stations in the Bronx, Brooklyn, Manhattan, and Queens. The project, using 800 kilometers of fiber-optic cable, will be completed by 1992. Fiber-optic cable and accessories for this network will be manufactured in Canada and the United States.[7]

Japan

Germanium metal production was 3,346 kilograms, a decrease of about 20% compared with 1988 metal production levels. Dioxide production also decreased from 13,883 kilograms in 1988 to 13,302 kilograms in 1989.[8]

Poland

Installation of an underwater fiber-optic cable between Poland and Denmark was started by Nordiske Kabel & Traadfabiken A/S of Denmark. The cable will connect the Danish island of Bornholm in the Baltic Sea with the settlement of Mielno near Koszalin, Poland. The 150-kilometer network system was scheduled for completion by 1990 and was expected to greatly upgrade Poland's communication capacity with the United States and Canada through Denmark via the United Kingdom. Total project cost was estimated at $4.5 million and will be jointly financed by Poland and the telecommunications authorities of Denmark, Finland, Norway, and Sweden.[9]

OUTLOOK

Abundant supplies of germanium materials on the market through 1989 could not be absorbed by a rather stagnant demand. Producers were forced to lower prices to maintain their share of the market. Germanium supplies are likely to remain high for the next 2 years, owing to larger availability of concentrates from Canada and resumed mining operations by Hecla Mining Co. at their recently acquired gallium-germanium Apex Mine in Utah.

Domestic short-term demand for germanium metal probably will fall below the 1989 level. A reduced spending rate for strategic programs, as a consequence of recent events in Eastern Europe, could have a negative impact on germanium consumption for infrared systems for conventional weaponry.

BACKGROUND

Germanium was recovered as a minor byproduct of the refining of base metal ores, and the potential supply of this metal, which was dependent on the level of zinc production, has historically exceeded demand.

Invention and development of the germanium transistor opened the path for the solid-state electronic field and, from 1950 through the early 1970's, provided an excellent market for germanium. Despite the continued growth of the electronics industry in the 1970's, germanium demand for transistors, diodes, and rectifiers declined. This decline was caused mainly by the increasing use of electronic-grade silicon, which was replacing germanium. However, the reduced demand for germanium in the electronics field was offset by a dramatic increase in demand for germanium in both infrared night vision systems and fiber-optic communication networks.

Definition, Grades, and Specifications

Germanium has a metallic appearance and is grayish white in color, lustrous, hard, and very brittle. It is a semiconductor, with electrical properties between those of a metal and an insulator.

The National Stockpile Purchase Specification P-114-R, December 16, 1989, for intrinsic germanium metal specifies an electrical resistivity of 50 ohm-centimeter at 20° C (40 ohm-centimeter at 25° C) over the entire ingot length.

Germanium is available commercially as a tetrachloride and high-purity oxide and in the form of zone-refined ingots, single-crystal bars, castings, doped semiconductors, optical materials, optical blanks, and other specialty products.

Industry Structure

Most germanium occurs as a minor constituent of certain base metal ores and coal deposits. Those producers that currently recover primary germanium for the most part depend on germanium-rich residues, mainly from zinc derived from past or present base metal smelting operations.

In the United States, Eagle-Picher's Quapaw, OK, Specialty Materials Div. has the capability of recovering primary germanium from zinc smelter residues. Eagle-Picher also reprocessed scrap. Kawecki Berylco Industries Inc., a division of Cabot Inc. in Revere, PA, and Atomergic Chemetals Co., Plainview, NY, produced germanium from reprocessed scrap and semirefined foreign material.

The Jersey Minière Zinc Co. in Clarksville, TN, continued to produce germanium-rich residues as a byproduct of processing zinc ores from its Gordonsville and Elmwood Mines. These residues were shipped to MHO in Belgium for germanium recovery and refining.

Little information was available on

the financial structure of U.S. and world germanium industries. Germanium refiners usually were involved in the production and sale of many different metals and specialty products.

Geology-Resources

Minerals in which germanium is concentrated are germanite, a sulfoarsenite of copper, iron, and germanium with an average of 5% germanium; argyrodite, a double sulfide of germanium and silver containing 5% to 7% germanium; renierite, a complex sulfide of copper, iron, germanium, tin, zinc, and arsenic with 6% to 8% germanium; and several other minerals such as canfieldite, utrabasite, itoite, and stottite. Primary germanium minerals are normally formed in sulfide mineralization processes at low-to-intermediate temperatures, and secondary varieties may result from supergene alteration of sulfide ore deposits.[10]

Currently, there are two major reserves of germanium in the United States. The largest is the recoverable germanium that occurs as a minor constituent of zinc sulfide ores in the middle Tennessee zinc district. The other major reserve of germanium is in southern Utah. Here the germanium is found in the iron oxide ore zone of a depleted copper mine.

There are no reliable germanium assay data available for many areas of the world. The U.S. and world resources could be expanded if germanium were to be recovered from ash and flue dusts resulting from the burning of certain coals for power generation.

Technology

Germanium is obtained commercially as a byproduct of base metal refining and extracting. Improvements have been developed, but the basic processes have remained virtually unchanged.

Regardless of the source, germanium raw materials are reacted with concentrated hydrochloric acid to form germanium tetrachloride, which is then purified by fractional distillation. The purified germanium tetrachloride is hydrolyzed with water to produce germanium dioxide, which is removed by filtration and dried. The dried germanium dioxide is reduced with hydrogen at about 760° C to a germanium metal powder, which is then melted and cast into metal bars. These bars are then zone-refined to produce intrinsic grade metal. This high-purity metal is mainly used for electronics and infrared optics. Zone refining produces polycrystalline germanium.[11]

Certain applications of germanium, such as gamma-ray detectors, require single-crystal germanium. Single crystals are produced by two methods, the horizontal pulling process or the vertical pulling process, also known as the Czochralski method.

More than 50% of the metal used during the manufacture of most electronic and optical devices is recycled as new scrap. As a result of the low unit use of germanium in microelectronic devices, very little germanium returns as old scrap.

TABLE 3

U.S. IMPORT DUTIES FOR GERMANIUM MATERIALS

Item	HTS No.	Most favored nation (MFN) Jan. 1, 1989	Non-MFN Jan. 1, 1989
Germanium: Waste and scrap	8112.30.3000	Free	Free
Germanium other: Unwrought	8112.30.6000	3.7% ad val.	25% ad val.
Germanium other: Other	8112.30.9000	5.5% ad val.	45% ad val.

Economic Factors

Table 3 shows import duties for germanium products, which became effective in January 1, 1989, under the new Harmonized Tariff Schedule of the United States.

Domestic producers are granted a depletion allowance of 14% on both domestic and foreign production of germanium.

Operating Factors

Germanium has little or no effect upon the environment because it usually occurs only as a trace element in some ores and carbonaceous materials. The small quantities used in commercial applications also pose no threat to the environment. Germanium compounds generally have a low order of toxicity, except for germanium tetrahydride which is considered toxic.

Based on a 1976 report, the energy requirements for the production of zone-refined germanium metal from zinc sulfide concentrates and scrap is 2,145 million British thermal units (Btu) per net ton of germanium ingot.

[1] Metals Week. V. 60, No. 40, Oct. 2, 1989, p. 3.

[2] American Metal Market. AT&T, Japanese Company Run Fiber-Optic Cable Under Pacific. V. 97, No. 125, June 28, 1989, p. 4.

[3] Laser Focus World. World News Breaks. V. 25, No. 4, Apr. 1989, p. 13.

[4] Photonics Spectra. Navy FO Market Poised for Growth. V. 23, No. 5, May 1989, pp. 46, 48.

[5] Where necessary, values have been converted from Belgian francs (BF) to U.S. dollars at the 1989 average exchange rate of BF39.4 = US$1.00.

[6] Photonics Spectra. Brazil Orders Philips Fibers. V. 23, No. 9, Sept. 1989, p. 74.

[7] American Metal Market. Canstar Gets Fiber-Optic Network Pact. V. 97, No. 51, Mar. 15, 1989, p. 4.

[8] Japan Metal Journal. V. 20, No. 13, Mar. 26, 1989, p. 2.

[9] Photonics Spectra. Fiber to Link Poland, Denmark. V. 23, No. 4, Apr. 1989, p. 62.

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[11] Adams, J. H. Germanium Compounds. Ch. in Encyclopedia of Chemical Technology. Kirk-Othmer, 3d ed., v. 11, 1983, pp. 791-802.

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